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ON THE PEROVSKITE-RELATED MATERIALS OF HIGH DIELECTRIC
 PERMITTIVITY WITH SMALL TEMPERATURE DEPENDENCE AND LOW
 DIELECTRIC LOSS

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Abstract Dielectric properties of quantum paraelectric materials, SrTiO_3 , CaTiO_3 and $(\text{La}_{1/2}\text{Na}_{1/2})\text{TiO}_3$, were presented and discussed since they show the titled dielectric properties in the lowest temperature range. In order to show our strategy to obtain the titled materials for microwave resonator applications, dielectric properties of several solid solution systems, SrTiO_3 - LaAlO_3 , Sr_2TiO_4 - SrLaAlO_4 and BaTiO_3 - $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{1/3})\text{O}_3$ were exemplified. Concerning about relaxor ferroelectric materials, it is pointed out that a drastic broadening of ferroelectric phase transitions in the KNbO_3 - BaTiO_3 and BaTiO_3 - $\text{Ba}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$ solid solution systems is caused by a strong local field fluctuation come from the randomly oriented permanent electric dipoles produced by the heterogeneous cationic charge distribution in the solid solution.

INTRODUCTION

With the rapid popularization of mobile communications on the microwave, the demands for dielectric resonator applications increase progressively. The materials with high dielectric constant, ϵ , small temperature coefficient of ϵ , $\tau_\epsilon \equiv \left(\frac{1}{\epsilon}\right)\left(\frac{d\epsilon}{dT}\right)$, and high Q value are desired for the application of microwave dielectric resonators. Several solid solution systems designed to approach the above dielectric properties are presented. Besides the mentioned materials, some quantum paraelectric materials and relaxor ferroelectric materials are given.

QUANTUM PARAELECTRIC MATERIALS

Quantum paraelectricity found in perovskite-type oxides SrTiO_3 ¹ may satisfy the titled dielectric properties only in the lowest temperature region - 4 K. However, "higher quantum paraelectricity" have been recently found in CaTiO_3 ², $(\text{La}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ ³ etc. Figure 1 shows the temperature dependence of dielectric constant for CaTiO_3 , $\text{Ca}_4\text{Ti}_3\text{O}_{10}$ and $(\text{La}_{1/2}\text{Na}_{1/2})\text{TiO}_3$. Since the thermal energy in $T = 1$ K corresponds to the photon energy $h\nu$ of microwave in $\nu = 20.8$ GHz, an excitation of optical vibrational mode in CaTiO_3 and $(\text{La}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ with microwave of $\nu \sim 20$ GHz is neglectable for the range 10 K - 25 K, where the values of ϵ are constants. This means that there do not exist thermal excitation of optical modes. Therefore, the dielectric loss in the microwave region can be small for CaTiO_3 and $(\text{La}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ at 10 K - 25 K. Table I lists the constants involved in the following Barrett formula⁴ for several perovskite-type oxides.

$$\epsilon = \frac{C}{\left(\frac{T_1}{2}\right) \coth\left(\frac{T_1}{2T}\right) - T_0}$$

High temperature quantum paraelectric materials are desired. The occurrence of high permittivity in perovskite-type titanates ATiO_3 ($A = \text{Pb}, \text{Ba}, \text{Cd}, \text{Sr}, \text{Ca}$) may be ascribed to an accidental coincidence of ionic masses $m(\text{Ti}^{4+}) = 3m(\text{O}^{2-}) = 48$, not only a pertinent space available for Ti^{4+} ions in the oxygen octahedral sites. These fortunate conditions

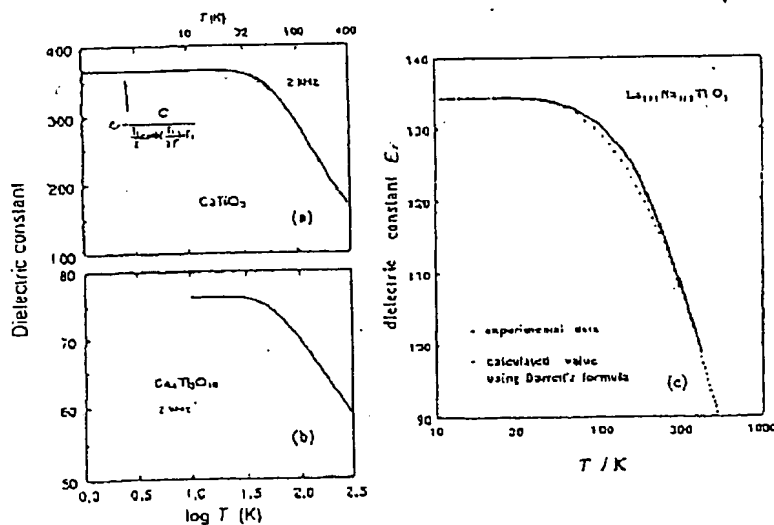


FIGURE 1 Temperature dependence of the dielectric constant of CaTiO_3 (a), $\text{Ca}_4\text{Ti}_3\text{O}_{10}$ (b) and $(\text{La}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (c).

TABLE I The constants involved in the Eyring formula for several perovskite-type oxides

| | ϵ_m | T_m^*/K | C/K | T_1/K | T_0/K |
|--|--------------------|-----------|-------------------|---------|---------------------|
| SrTiO_3 | 2.00×10^4 | -4 | 9.0×10^4 | 84 | 38 |
| CaTiO_3 | 3.70×10^2 | -30 | 7.7×10^4 | 104 | -1.59×10^2 |
| $(\text{Na}_{1/2}\text{La}_{1/2})\text{TiO}_3$ | 1.34×10^2 | -32 | 1.2×10^5 | 180 | -7.70×10^2 |
| $(\text{Na}_{1/2}\text{Sm}_{1/2})\text{TiO}_3$ | 1.13×10^2 | -40 | 3.1×10^5 | 205 | -2.66×10^2 |
| $(\text{Na}_{1/2}\text{Gd}_{1/2})\text{TiO}_3$ | 1.02×10^2 | -55 | 2.9×10^5 | 261 | -2.69×10^2 |

*: The onset temperature that ϵ becomes maximum and constant.

may facilitate the lattice vibration of Slater soft mode in ATiO_3 . Actually, three ferroelectrics, PbTiO_3 ($T_c = 763$ K), BaTiO_3 ($T_c = 393$ K), CdTiO_3 ($T_c = 55$ K) present in the ATiO_3 series with heavier masses $m(\text{A}^{2+}) > m(\text{TiO}_3) = 96$. This evidence suggests a coexistence of the Last and Slater soft modes. In the lighter titanates SrTiO_3 and CaTiO_3 , tilts or deformation of oxygen octahedra occur at certain higher temperatures than the temperatures where softening of the Slater or Last mode can occur. The tilts or deformation of oxygen octahedra changes the reduced masses and force constants of soft modes for ferroelectricity, hardens the modes, and results in a quantum paraelectricity.

TOWARD MICROWAVE DIELECTRIC MATERIALS

Since the materials with the titled dielectric properties are quite rare in nature, we have intended to get them under the strategy by forming a solid solution system from the following two classes of isostructural materials.

The material of class I is the paraelectric material with a purposely high ϵ value and a negative temperature coefficient ($\tau_r < 0$) around the room temperature for practical use.

The material of class I may have ferroelectric or antiferroelectric phase transitions much below the room temperature. It is believed that the domain wall motion is sensitive under the microwave frequency region and ready to lower the Q value in the ferroelectric materials. Therefore, in order to avoid a formation of ferroelectric domains in the resultant solid solution system, the material of class II should be a paraelectric or an antiferroelectric materials with a purposely high ϵ value and a positive temperature coefficient ($\tau_r > 0$). A quantum paraelectric perovskite SrTiO_3 ¹ was chosen as the material of class I and an antiferrodistortive perovskite LaAlO_3 ^{5,6}, whose transition temperature locates at $T_N = 810$ K, was chosen as the material of class II. The dielectric properties of the SrTiO_3 - LaAlO_3 solid solution system are shown in Fig.2. Table 2 lists the dielectric data versus composition of the solid solution system. We have studied the

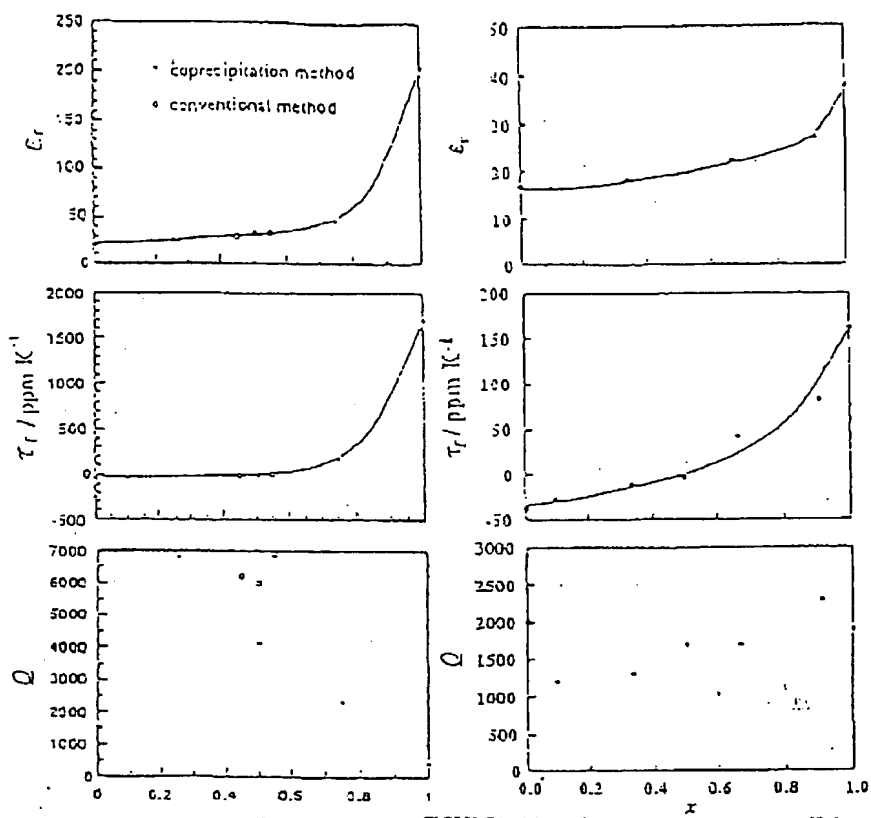


FIGURE 2 Dielectric constant, temperature coefficient and Q value in $x\text{SrTiO}_3 \cdot (1-x)\text{LaAlO}_3$.

FIGURE 3 Dielectric constant, temperature coefficient and Q value in $(1-x)\text{Sr}_2\text{TiO}_4 \cdot x\text{SrLaAlO}_4$.

dielectric properties of Ruddlesdon-Popper series compound $\text{Sr}_{n+1}\text{Ti}_n\text{O}_{5n+1}$ ($n = 1, 2, \dots, \infty$). It is found that SrTiO_3 shows the largest ϵ_r while Sr_2TiO_4 shows the smallest ϵ_r . The dielectric properties of Ruddlesdon-Popper solid solution $\text{Sr}_2\text{TiO}_4\text{-SrLaAlO}_4$ at microwave range are shown in Fig.3. The ϵ_r of $\text{Sr}_2\text{TiO}_4\text{-SrLaAlO}_4$ system are lower than that of $\text{SrTiO}_3\text{-LaAlO}_3$ system. Similar tendency as in Fig.2 can be seen in Fig.3. $\text{SrTiO}_3\text{-LaAlO}_3$ system has very good dielectric properties at microwave range, it shows high Q value, low τ_f and purposely high ϵ value. The practical application of $\text{SrTiO}_3\text{-LaAlO}_3$ is expectable.

DIFFUSE FERROELECTRIC PHASE TRANSITION IN RELAXORS

Concerning the origin of relaxor materials^{7,8}, it is pointed out that the broadening of the

TABLE II Microwave dielectric properties of $x\text{SrTiO}_3 - (1-x)\text{LaAlO}_3$

| x | ϵ | Q | f/GHz | Qf/GHz | $\tau_f^{**}/\text{ppm K}^{-1}$ |
|-------|------------|------|----------------|-----------------|---------------------------------|
| 0.00* | 21 | 1500 | 8.6 | 12900 | -49 |
| 0.25* | 24 | 6800 | 11.1 | 74800 | -35 |
| 0.45 | 29 | 6200 | 9.8 | 60800 | -21 |
| 0.50* | 31 | 4100 | 9.6 | 39400 | 0 |
| 0.50 | 33 | 6000 | 9.0 | 54000 | -13 |
| 0.55 | 34 | 6900 | 8.8 | 60720 | -8 |
| 0.75* | 46 | 2300 | 10.7 | 24600 | 170 |
| 1.00* | 204 | 400 | 10.6 | 4200 | 1700 |

*: by coprecipitation from aqueous solutions

**: $\tau_f = \left(\alpha + \frac{1}{2}\epsilon \right)$; α : linear thermal expansion coefficient τ_f : temperature coefficient of resonant frequency

ferroelectric phase transitions versus composition is more drastic in the $\text{KNbO}_3\text{-BaTiO}_3$ ⁹ and $\text{BaTiO}_3\text{-Ba(Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$ ¹⁰ solid solution systems than in the $\text{KNbO}_3\text{-KTaO}_3$ ¹¹ and $\text{BaTiO}_3\text{-BaSnO}_3$ ¹⁰ solid solution systems, respectively. The cause of this diffuse ferroelectric phase transitions in the $\text{KNbO}_3\text{-BaTiO}_3$ and $\text{BaTiO}_3\text{-Ba(Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$ systems is discussed and gets a conclusion that it originates from the randomly oriented various permanent electric dipoles produced by the random distribution of the cationic charge over the octahedral and the cuboctahedral sites in the former solid solution system. The random distribution of the cationic charge gives a strong fluctuation upon the local fields of every sites for cations and anions, and results in a violent damage to the long-range cooperative ferroelectric interactions.

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